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(54) The Use of Ethylene Terpolymers as Additives in Mineral Oil and Miniral Oil Distillates

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Abstract of Disclosure

An additive for mineral oils and/or mineral oi fractions comprising a terpolymer containing 0.5 to 20% by weigh diisobutylene, 20-35% by weight vinyl acetate, both based c total terpolymer, and ethylene, said terpolymer having an averac molecular weight of 500 to 10,000.

Compositions containing the additive and methods c reducing both the pour point and the cold filter plug point c the oils and fractions, as well as a method of preparation of th terpolymers, are also disclosed.

1271895

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPER
PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An additive for mineral oils and/or mineral oil frac comprising a terpolymer containing 0.5 to 20% by w diisobutylene, 20-35% by weight vinyl acetate, both based on terpolymer, and ethylene, said terpolymer having an av molecular weight of 500 to 10,000.

2. The additive of Claim 1 wherein there is a 1 to 15% by w of said diisobutylene based on said terpolymer.

3. The additive of Claim 1 wherein said terpolymer has an a molecular weight of 1,000 to 5,000.

4. The additive of Claim 1 wherein said terpolymer viscosity of 100 to 1,000 mPa's at 140°C.

5. The additive of Claim 1 wherein there is 22 to 30% by of said vinyl acetate based on said terpolymer.

6. The additive of Claim 1 wherein there are 7 to 15 CH_3 in side chains per 100 Ch_2 groups.

7. A method of preparation of the terpolymers of C comprising polymerizing 35 to 75% by weight of said ethylen

1271895

30 by weight of said diisobutylene, and 20 to 35% by weight of vinyl acetate, all based on said terpolymer.

8. The method of Claim 7 wherein said polymerizing takes under a pressure of at least 50 mPa and a temperature of 1 350°C in the absence of an organic solvent.

9. A composition comprising at least one said mineral oil a at least one said mineral oil fraction and 0.001 to 2.0% by w of the additive of Claim 1.

10. The composition of Claim 9 wherein there is present 0. 0.5% by weight of said additive.

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Ethylene Terpolymer Additives for Mineral Oil and Mineral Oil Distillates

The present invention relates to the use of terpolyme of ethylene, diisobutylene and vinylacetate to improve tl flowability and the low temperature behaviour of mineral oil ai mineral oil distillates.

Mineral oils such as crude oil, diesel fuel or fuel o contain varying amounts of long-chain paraffins (waxes) dissolv in them which crystallize out at low temperatures. This lea to solid deposits which often cause breakdowns during tl recovery, transportation and use of such oils. Thus, tl operability of crude oil conveyance and transportation faciliti can be impaired to such a degree that they fail completely. Wi diesel engines and firing plants the filter can become blocke preventing accurate dosage of the fuels and finally resulting a complete breakdown of the equipment.

This undesirable formation of solid deposits counteracted by additives which prevent the paraffin crysta from forming and stop the viscosity of the oils from increasin

The flow and low temperature behaviour of mineral oils and mineral oil distillates is measured by the pour point and the cold filter plugging point (CFP point). The pour point (determined in accordance with DIN 51 597) is the lowest temperature at which a mineral oil or mineral oil distillate can still just flow. The cold filter plugging point (determined in accordance with DIN 51 428) represents the limit of filterability. For economic reasons it is of interest to find one single additive which favorably influences both the pour point and the cold filter plugging point.

Typical pour point reducers and flow improvers for crude oils and middle distillates are ethylene copolymers with carboxylic acid esters of vinyl alcohol. Of these copolymers ethylene/vinylacetate has proved to be particularly successful. Such copolymers and their applications are described, for example, in DE-PS 1 914 756. They are generally produced by copolymerization of the corresponding monomers in autoclaves at temperatures of 80 to 150° C and pressures of 5 to 15 MPa in the presence of peroxides as initiators and organic solvents as reaction media.

A disadvantage of the ethylene/vinylacetate copolymers is that, although they improve the CFP point of middle distillates, they only slightly reduce the pour point.

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The task therefore consisted in preparing additives for mineral oils which appreciably reduce both the CFP point and the pour point.

The invention consists in the use of terpolymers which not only contain ethylene but also 0.5 to 20% by weight diisobutylene and 20 to 35% by weight vinylacetate and which have an average molecular weight of 500 to 10,000 as additives in mineral oils and mineral oil distillates.

Surprisingly, the problem is solved by the use of the particular terpolymers of the present invention. It was impossible to foresee that terpolymers of ethylene, diisobutylene and vinylacetate would appreciably reduce both the CFP point and the pour point of mineral oils and mineral oil distillates.

It is recognized that terpolymers of ethylene, isoolefins (in particular isobutene), and vinylacetate as such are known as flow improvers from the EP 0 099 646 A1. However, these products have little effect as both pour point and CFP point reducers. The ethylene terpolymers employed in accordance with the invention contain 0.5 to 20% by weight diisobutylene. Terpolymers wherein the proportion of Co-olefins is 1 to 15% by weight (based on the terpolymer) have proven to be particularly successful.

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In the terpolymer employed in accordance with the invention, the proportion of vinylacetate is 20 to 35% by weight, a proportion of 22 to 30% by weight is preferred, based on the terpolymer.

The average molecular weight of the terpolymers of the invention, measured in a steam phase osmometer with toluene as a solvent, is 500 to 10,000; polymers with a molecular weight of 1,000 to 5,000 are preferred.

In another preferred embodiment of the invention terpolymerisates are used whose melt viscosity (measured at 140°C) is 100 to 1,000 mPa x sec. The melt viscosity is determined in a rotation viscosimeter in accordance with the German Standard DIN 53019.

The ethylene/diisobutylene(vinylacetate terpolymers contain branchings which are due to the incorporation of diisobutylene and ethylene in the macromolecule. For every 100 CH_2 groups, the terpolymers carry 6 to 20 CH_3 groups in the side chains and which do not originate from the vinylacetate. In accordance with the invention, the terpolymers preferably contain 7 to 15 CH_3 groups in the side chains per 100 CH_2 groups.

The terpolymers which are employed in accordance with the invention are prepared from mixtures of ethylene, diisobutylene, and vinylacetate which are polymerized in the presence of radical-forming initiators (such as peroxides)

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at pressures above 50 mPa and at temperatures of 150 to 350°C in the absence of organic solvents. The molecular weights of the terpolymers are preferably determined by the diisobutylene. Other molecular weight controllers such as hydrocarbons, aldehydes and ketones can also be used; however, they should be present in amounts of 1 to 5% by weight based on the monomer mixture. Propionaldehyde is particularly suitable as a molecular weight controller. Monomer mixtures containing 79 to 20% by weight ethylene, 1 to 40% by weight diisobutylene and 20 to 40% by weight vinylacetate are among those suitable for polymerization.

Generally speaking, the terpolymer is added to the mineral oils or mineral oil fractions in the form of a 40 to 60% by weight solution in an aliphatic or aromatic hydrocarbon or in a hydrocarbon mixture. Kerosene has, for example, proven to be very suitable as a solvent. The amount of polymer based on the mineral oil or mineral oil fraction should be 0.001 to 2%, preferably 0.005 to 0.5%, by weight. The terpolymer can be used alone or together with other additives; for example, with dewaxing agents, corrosion inhibitors, antioxidants or sediment inhibitors.

The use of ethylene/diisobutylene/vinylacetate terpolymers according to the invention as additives for mineral oils and mineral oil distillates is explained in detail in the following examples:

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Examples A - C relate to the manufacture and properties of ethylene/diisobutylene/vinylacetate terpolymers. Examples D - F describe the manufacture and properties of polymers which are cited as comparative substances. Data on the efficiency of the terpolymers employed as additives in mineral oil and mineral oil distillates in accordance with the invention are compiled in examples 1 - 3. The data are compared with the figures obtained for the comparative substances in examples 4 - 6.

Examples A - C: Manufacture of Ethylene/diisobutylene Vinylacetate Terpolymers.

Ethylene, diisobutylene (technical diisobutylene with about 75% by weight 2,4,4-trimethylenpentene-1) and vinylacetate are continuously polymerized in an autoclave. The monomer mixture is fed into the autoclave at the reaction pressure after the amount of peroxide required to maintain polymerization has been added as a solution in a petrol fraction. The residence period is about 80 seconds. The manufacture of the terpolymers listed in examples D - F takes place in the same manner. The polymerization conditions used and the characteristic properties of the polymers obtained are listed in Table 1.

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The vinylacetate content of the polymers is determined by the pyrolysis method. This involves taking 200 mg of the polymer and heating it with 300 mg of pure polyethylene in a pyrolysis flask for 5 minutes to a temperature of 450°C. The cracked gases are collected in a 250ml round flask. The acetic acid formed is reacted with a NaI/KIO_3 solution and the iodine thus released is titrated with a $Na_2S_2O_3$ solution.

The degree of branching of the polymers is determined by means of H-NMR spectroscopy. In the following examples, the degree of branching is understood to be the number of CH_3 groups per 100 CH_2 groups, except for those CH_3 groups which originate with the acetate group. The viscosity is measured with a Rotovisco System MV II (manufacturer: Haake, Karlsruhe) at a temperature of 140°C. The diisobutylene content in the polymer is determined by means of 13 C-NMR spectroscopy.

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Table 1: Manufacture and properties of the ethylene/diisobutylene/vinylacetate terpolymers

Example		A	B	C	D	E	F
Reaction conditions							
Pressure	(MPa)	150	150	150	150	150	150
Temperature	(°C)	200	200	230	160	230	230
Feed mixtures							
ethylene	(weight %)	56.5	60.4	61.5	65.3	70.4	70.9
isobutylene	(weight %)	-	-	-	-	15.0	14.9
diisobutylene	(weight %)	19.8	9.8	10.0	26.5	-	-
vinylacetate	(weight %)	23.7	28.1	27.2	19.1	15.1	25.4
initiator	(weight ppm)	7100	226	85			
propionaldehyde (As a Controller)	(weight ppm)	-	1.7	1.3			
Characteristic features of the polymerisates							
branching (CH_3/100 CH_2)		13.2	7.6	8.2	16.4		
diisobutylene	(weight %)	5.6	3.4	3.4	8.1		
vinylacetate	(weight %)	23.0	25.7	25.4	18.2	14.6	24.2
viscosity at 140°C	(mPa x s)	210	240	254	550	220	205

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Examples 1 - 6

In the following examples 1 - 6, the efficiencies of the use of various ethylene/diisobutylene/vinylacetate and ethylene/isobutylene/vinylacetate terpolymers are described as additives in mineral oils and mineral oil distillates. The CFPP test (cold filter plugging point) and determination of the pour points, measure this characteristic. Examples 1 - 3 are terpolymers in accordance with the invention; examples 4 - 6 relate to terpolymers which are not covered by the invention and serve as a comparison. The test is performed in accordance with DIN 51428 and is also published in the Journal of the Institute of Petroleum, volume 52, June 1966, pages 173 to 185. The pour point is measured in accordance with DIN 51597.

Three middle distillates M1, M2 and M3 were tested and their properties compiled in Table 2.

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TABLE 2

Characteristic data of the middle distillates

	M 1	M 2	M3
analysis by boiling (°C)			
boiling begin	180	209	182
5%	202	281	213
50%	297	289	281
90%	357	356	349
boiling end	357	368	370
pour point (°C)	- 6	- 9	-
CFPP point (°C)	+ 1	- 1	- 6

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Table 3: Efficiency of the ethylene/diisobutylene/vinylacetate terpolymers (Examples 1 - 3) used in accordance with the invention as additives in mineral oil fractions as compared with other terpolymers (Examples 4-6)

Example	Polymer from example	concentration (ppm) *	CFPP figure (°C) M 1	CFPP figure (°C) M 2	CFPP figure (°C) M 3	Pour Point (°C) M 1	Pour Point (°C) M 2
1	A	100	- 7	- 4	- 10	-	-
		300	-	- 4	-	-	-
		400	- 12	- 10	-	- 20	- 23
2	B	100	- 9	- 4	- 13	-	-
		300	-	- 4	-	-	-
		400	- 14	- 7	-	- 23	- 23
3	C	100	- 8	- 5	- 13	-	-
		300	-	- 9	-	-	-
		400	- 14	- 9	-	- 21	- 22
4	D	100	- 6	- 4	- 10	-	-
		300	-	- 5	-	-	-
		400	- 10	- 8	-	- 17	- 16
5	E	100	- 2	- 3	- 9	-	-
		300	-	- 5	-	-	-
		400	- 4	- 5	-	- 12	- 18
6	F	100	+ 1	- 1	- 8	-	-
		300	-	- 4	-	-	-
		400	0	- 4	-	- 18	- 24

* weight ppm related to the middle distillate

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The results compiled in Table 3 show that only waxy terpolymers which contain diisobutylene qualitatively as a termonomer and 20 to 35% by weight vinylacetate quantitatively reduce both the pour point and the CFP point to the extent desired in practice.

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